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REGULAR ARTICLE

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Average electron momenta in many-electron atoms

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Abstract In many-electron atoms, the average electron momentum $\langle p\rangle$ represents the mean momentum of a single electron when all the electron motions are averaged. If any two electrons are considered simultaneously, however, the average momentum $\langle p\rangle$ splits into two different momenta, low momentum $\langle p_<\rangle$ and high momentum $\langle p_>\rangle$. For the 102 atoms He through Lr in their ground states, the momenta $\langle p_<\rangle$ and $\langle p_>\rangle$ are systematically examined at the Hartree–Fock limit level. It is also shown that the sum $\langle p_>\rangle + \langle p_<\rangle$ and the difference $\langle p_>\rangle - \langle p_<\rangle$ of the two momenta constitute upper and lower bounds to the electron-pair relative momentum $\langle p_{12}\rangle = \langle|\mathbf{p}_1 - \mathbf{p}_2|\rangle$ and to the electron-pair center-of-mass momentum $\langle P\rangle = \langle|\mathbf{p}_1 + \mathbf{p}_2|/2\rangle$. The tightness of the bounds is discussed for the 102 atoms.

Keywords Electron momenta · Splitting · Electron-pair momenta · Upper and lower bounds · Many-electron atoms

1 Introduction

In many-electron atoms, the average distance of an electron from the nucleus is given by the average electron radius $\langle r\rangle$, which represents the mean radius of an electron orbital when all the electron motions are averaged and only a single electron is focused upon. If any two electrons are considered simultaneously, however, it has recently been shown [1] that the average radius $\langle r\rangle$ splits into inner $\langle r_<\rangle$ and outer $\langle r_>\rangle$ radii to reduce the electron-electron repulsion. The splitting of the average subshell radius $\langle r\rangle_{nl}$ into the inner $\langle r_<\rangle_{nl}$ and outer $\langle r_>\rangle_{nl}$ radii was also discussed in Ref. [2], where n and l are the principal and azimuthal quantum numbers.

In the present paper, we study the splitting of the average electron momentum $\langle p\rangle$ into low $\langle p_<\rangle$ and high $\langle p_>\rangle$ momenta, when any two electrons are considered explicitly. It is also shown that the sum $\langle p_>\rangle + \langle p_<\rangle$ and the difference $\langle p_>\rangle - \langle p_<\rangle$ of the two momenta constitute upper and lower bounds, respectively, to the electron-pair relative momentum $\langle p_{12}\rangle = \langle|\mathbf{p}_1 - \mathbf{p}_2|\rangle$ as well as to the electron-pair center-of-mass momentum $\langle P\rangle = \langle|\mathbf{p}_1 + \mathbf{p}_2|/2\rangle$. Numerical results are discussed for the ground-state atoms He through Lr at the Hartree–Fock limit level. Hartree atomic units are used throughout.

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2 Splitting of average electron momentum

In momentum space, the average radius of an electron orbital is given by the average electron momentum $\langle p\rangle$ defined by

$$\langle p\rangle = \frac{1}{N}\int_0^\infty \mathrm{d}p\, pI(p)\,, \tag{1}$$

where $I(p)$ is the single-electron radial momentum density (see, e.g., Ref. [3]), normalized to N, the number of electrons, and is related to the experimental Compton profile $J(q)$ through $I(p) = -2p[\mathrm{d}J(q)/\mathrm{d}q]_{q=p}$. The quantity $\langle p\rangle$ represents the mean radius of an electron momentum orbital when all the electron motions are averaged. If any two electrons are considered simultaneously, however, the electrons prefer different momenta, low momentum $p_<$ and high momentum $p_>$, to avoid each other in momentum space. As they are the position-space counterparts [1], the average low $\langle p_<\rangle$ and high $\langle p_>\rangle$ momenta are defined by

$$\langle p_<\rangle = \frac{2}{N(N-1)}\int_0^\infty \mathrm{d}p_1 \int_0^\infty \mathrm{d}p_2\, p_<\, I_2(p_1, p_2)\,, \tag{2a}$$

$$\langle p_>\rangle = \frac{2}{N(N-1)}\int_0^\infty \mathrm{d}p_1 \int_0^\infty \mathrm{d}p_2\, p_>\, I_2(p_1, p_2)\,, \tag{2b}$$

where $p_< = \min(p_1, p_2)$, $p_> = \max(p_1, p_2)$, and $I_2(p_1, p_2)$ is the two-electron radial momentum density (see, e.g., Ref. [4]) normalized to $N(N-1)/2$, the number of electron pairs.

The single-electron radial momentum density $I(p)$ that appeared in Eq. (1) is obtained from $I_2(p_1, p_2)$ by $I(p) = [2/(N-1)]\int_0^\infty \mathrm{d}p_2 I_2(p, p_2)$. Since $p_< + p_> = p_1 + p_2$ and $p_> - p_< = |p_1 - p_2|$, we find

$$\langle p_< \rangle = \langle p \rangle - \frac{1}{2}\langle |p_1 - p_2| \rangle \,, \tag{3a}$$

$$\langle p_> \rangle = \langle p \rangle + \frac{1}{2}\langle |p_1 - p_2| \rangle \,, \tag{3b}$$

as well as $(\langle p_< \rangle + \langle p_> \rangle)/2 = \langle p \rangle$, where

$$\langle |p_1 - p_2| \rangle = \frac{2}{N(N-1)} \int_0^\infty \mathrm{d}p_1 \int_0^\infty \mathrm{d}p_2 |p_1 - p_2| I_2(p_1, p_2). \tag{4}$$

Equation (3) implies that the explicit consideration of any two electrons splits the momentum $\langle p \rangle$ into the momenta $\langle p_< \rangle$ and $\langle p_> \rangle$ separated by $\langle |p_1 - p_2| \rangle$. In other words, the traditional average momentum $\langle p \rangle$ consists of two components, the low $\langle p_< \rangle$ and high $\langle p_> \rangle$ momenta, which can be more informative for electronic structure studies than $\langle p \rangle$ itself.

3 Bounds to electron-pair relative and center-of-mass momenta

Two important properties appearing in the electron-pair intracule (relative motion) and extracule (center-of-mass motion) studies in momentum space (see, e.g., Ref. [5]) are the electron-pair relative momentum (or the first intracule moment) $\langle p_{12} \rangle = \langle |\mathbf{p}_1 - \mathbf{p}_2| \rangle$ defined by

$$\langle p_{12} \rangle = \frac{2}{N(N-1)} \int \mathrm{d}\mathbf{p}_1 \int \mathrm{d}\mathbf{p}_2 |\mathbf{p}_1 - \mathbf{p}_2| \Gamma(\mathbf{p}_1, \mathbf{p}_2) \,, \tag{5a}$$

and the electron-pair center-of-mass momentum (or the first extracule moment) $\langle P \rangle = \langle |\mathbf{p}_1 + \mathbf{p}_2|/2 \rangle$ defined by

$$\langle P \rangle = \frac{2}{N(N-1)} \int \mathrm{d}\mathbf{p}_1 \int \mathrm{d}\mathbf{p}_2 \frac{|\mathbf{p}_1 + \mathbf{p}_2|}{2} \Gamma(\mathbf{p}_1, \mathbf{p}_2) \,, \tag{5b}$$

where $\Gamma(\mathbf{p}_1, \mathbf{p}_2)$ is the spinless two-electron density function in momentum space (see, e.g., Ref. [5]) normalized to $N(N-1)/2$. The two-electron radial momentum density $I_2(p_1, p_2)$ that appeared in Eq. (2) is obtained from $\Gamma(\mathbf{p}_1, \mathbf{p}_2)$ as $I_2(p_1, p_2) = p_1^2 p_2^2 \int \mathrm{d}\Omega_1 \mathrm{d}\Omega_2 \Gamma(\mathbf{p}_1, \mathbf{p}_2)$, where (p_i, Ω_i) are the polar coordinates of the momentum vector $\mathbf{p}_i$.

The relative momentum $p_{12} = |\mathbf{p}_1 - \mathbf{p}_2|$ of two electrons with momenta $\mathbf{p}_1$ and $\mathbf{p}_2$ is explicitly written as

$$p_{12} = (p_1^2 + p_2^2 - 2p_1 p_2 \cos\,\theta_{12})^{1/2} \,, \tag{6}$$

where $\theta_{12} (0 \le \theta_{12} \le \pi)$ is the angle spanned by the vectors $\mathbf{p}_1$ and $\mathbf{p}_2$. As $-1 \le \cos\theta_{12} \le +1$, it immediately follows that

$$|p_1 - p_2| \le p_{12} \le (p_1 + p_2) \,, \tag{7a}$$

which is rewritten in terms of the variables $p_< = \min(p_1, p_2)$ and $p_> = \max(p_1, p_2)$ as

$$(p_> - p_<) \le p_{12} \le (p_> + p_<) \,. \tag{7b}$$

We then have an inequality,

$$(\langle p_> \rangle - \langle p_< \rangle) \le \langle p_{12} \rangle \le (\langle p_> \rangle + \langle p_< \rangle) \,, \tag{8}$$

which implies that the sum $\langle p_> \rangle + \langle p_< \rangle$ of the high and low momenta is an upper bound, whereas the difference $\langle p_> \rangle - \langle p_< \rangle$ is a lower bound, to the electron-pair relative momentum $\langle p_{12} \rangle$. The width of the two bounds is twice the low momentum, $2\langle p_< \rangle$, and the arithmetic mean of the bounds is the high momentum, $\langle p_> \rangle$.

On the other hand, the center-of-mass momentum $P = |\mathbf{p}_1 + \mathbf{p}_2|/2$ of two electrons with $\mathbf{p}_1$ and $\mathbf{p}_2$ is given by

$$P = \frac{1}{2}(p_1^2 + p_2^2 + 2p_1 p_2 \cos\,\theta_{12})^{1/2} \,. \tag{9}$$

Therefore, discussion analogous to that for p_{12} results in another inequality,

$$\frac{\langle p_> \rangle - \langle p_< \rangle}{2} \le \langle P \rangle \le \frac{\langle p_> \rangle + \langle p_< \rangle}{2} \,. \tag{10}$$

By means of the low $\langle p_< \rangle$ and high $\langle p_> \rangle$ momenta, the electron-pair center-of-mass momentum $\langle P \rangle$ is also bounded from above and below. The bounds are just half values of those for $\langle p_{12} \rangle$. Then, the width of the bounds is $\langle p_< \rangle$ and the arithmetic mean of the two bounds is $\langle p_> \rangle/2$. The results are in accord with the literature observation [6] that $\langle p_{12} \rangle \cong 2\langle P \rangle$.

4 Numerical results and discussion

We first examine the splitting of $\langle p \rangle$ into $\langle p_< \rangle$ and $\langle p_> \rangle$ for the 102 atoms He through Lr in their ground states [7]. For this purpose, we have performed numerical Hartree–Fock calculations of the three momenta, using a modified version of the MCHF72 program [8]. The calculated $\langle p \rangle$ values have been verified by comparison with the literature values [9], except the Bk and Lr atoms for which different states were considered in Ref. [9].

The results are plotted in Fig. 1a as a function of atomic number Z. All the momenta $\langle p_< \rangle$, $\langle p \rangle$, and $\langle p_> \rangle$ show a trend to increase as Z increases. The splitting of $\langle p \rangle$ into $\langle p_< \rangle$ and $\langle p_> \rangle$ is smallest at $Z = 2$ (He) and largest at $Z = 103$ (Lr), where the values of $\langle |p_1 - p_2| \rangle$ are 0.930 and 17.040, and the ratios $\langle p_> \rangle/\langle p_< \rangle$ are 1.996 and 3.460, respectively. In the case of the Lr atom, the low $\langle p_< \rangle$ and high $\langle p_> \rangle$ momenta are 55.2% smaller and larger than the usual average momentum $\langle p \rangle$, respectively. When Z increases, the high momentum $\langle p_> \rangle$ increases smoothly from 1.865 at $Z = 2$ to 23.967 at $Z = 103$. On the other hand, the low momentum $\langle p_< \rangle$ distributes between 0.744 ($Z = 3$) and 6.926 ($Z = 103$), and is found to show a small periodical structure reflecting the valence electronic configuration of atoms. To clarify this, we have examined for $3 \le Z \le 103$ the momentum increments defined by the momentum values at Z subtracted by the corresponding values at $Z - 1$, and plotted them in Fig. 1b. In contrast to

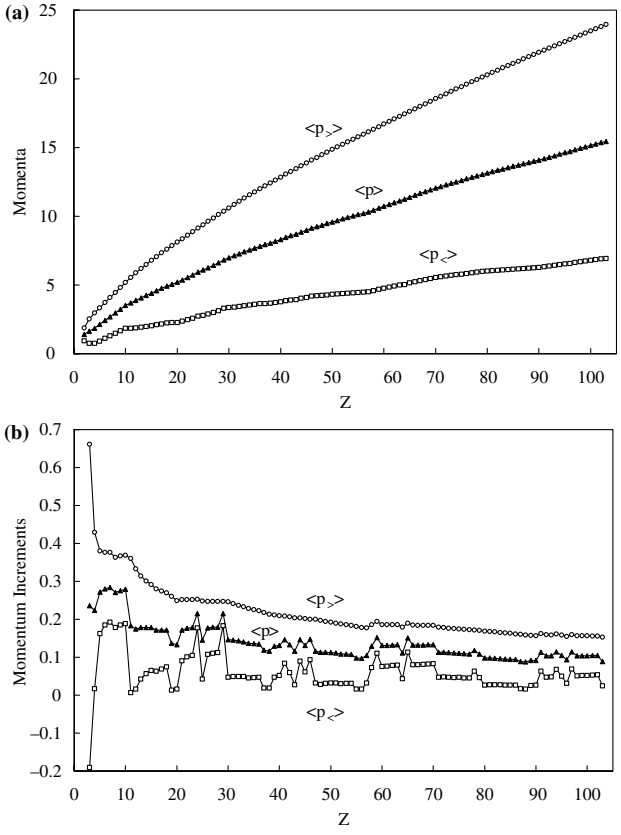

Fig. 1 The Hartree–Fock average momenta as a function of Z. **a** Momenta $\langle p_< \rangle$, $\langle p \rangle$, and $\langle p_> \rangle$. **b** Momentum increments

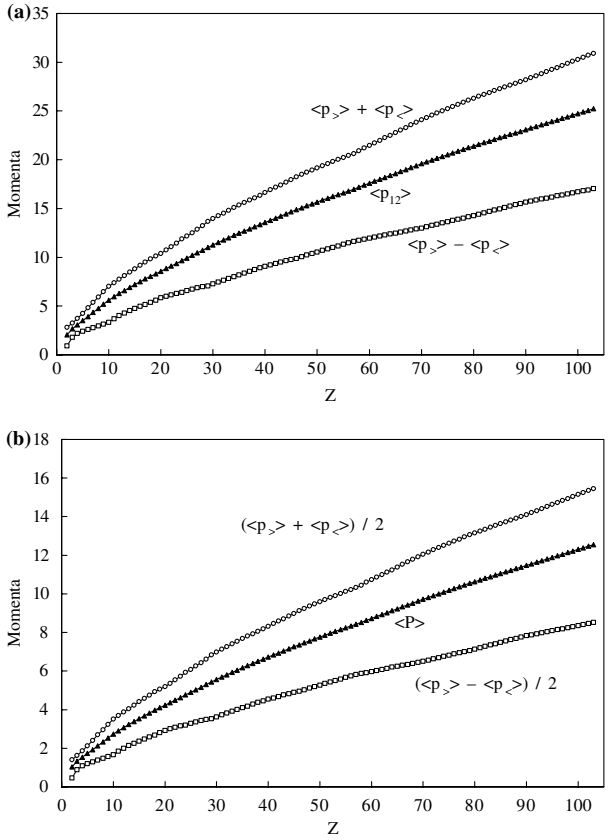

Fig. 2 The upper and lower bounds to the electron-pair momenta as a function of Z. **a** Relative momentum $\langle p_{12} \rangle$. **b** Center-of-mass momentum $\langle P \rangle$

the high momentum, the low momentum clearly shows the change in the valence configuration. Two typical cases are: (i) The group 1 or 2 atoms with the valence s or s^2 configuration have local minima in the low momentum increments. (ii) The transition atoms with valence sd^n configurations have larger increments than the neighboring atoms with s^2d^n configurations. In Fig. 1a, 1b, the average momentum $\langle p \rangle$ lies at the center of the low and high momenta as $\langle p \rangle$ is just the arithmetic mean of $\langle p_< \rangle$ and $\langle p_> \rangle$.

We next discuss the tightness of the upper and lower bounds derived in the previous section. The required relative momenta $\langle p_{12} \rangle$ were taken from Ref. [10] for $Z = 2$–54 and from Ref. [11] for $Z = 55$–103. The center-of-mass momenta $\langle P \rangle$ were reported in Ref. [6] for $Z = 2$–54 and in Ref. [11] for $Z = 55$–103. For the Bk ($Z = 97$) and Lr ($Z = 103$) atoms, however, the assignment of the ground electronic configurations and LS terms has been updated [7] after publication of Ref. [11]. Accordingly, the $\langle p_{12} \rangle$ and $\langle P \rangle$ values of these two atoms have been recomputed in this study, based on the methods developed in Refs. [6, 10].

The upper and lower bounds are plotted in Fig. 2a for $\langle p_{12} \rangle$ and in Fig. 2b for $\langle P \rangle$ as a function of Z. In Fig. 2a, we confirm numerically that the electron-pair relative momentum $\langle p_{12} \rangle$ is bounded by the sum $\langle p_> \rangle + \langle p_< \rangle$ and the difference $\langle p_> \rangle - \langle p_< \rangle$ for any atom. When averaged over the 102 atoms, the upper bound is 22.78% larger than $\langle p_{12} \rangle$ with minimum 20.84% (at $Z = 4$) and maximum 35.96% (at $Z = 2$) differences. The lower bound is 33.54% smaller than $\langle p_{12} \rangle$ on average, with the minimum 28.66% (at $Z = 4$) and maximum 54.81% (at $Z = 2$) differences. Figure 2b demonstrates the inequality (Eq. 10) numerically. Due to the approximate proportionality relation [6] $\langle p_{12} \rangle \cong 2\langle P \rangle$, Fig. 2b for the electron-pair center-of-mass momentum $\langle P \rangle$ is very similar to Fig. 2a for $\langle p_{12} \rangle$, except for the ordinates. In the case of center-of-mass momenta, however, the upper bound is 24.01% larger and the lower bound is 32.88% smaller than $\langle P \rangle$, when averaged over the 102 atoms. (For both bounds to $\langle P \rangle$, the values and locations of the minimum and maximum differences are same as those for $\langle p_{12} \rangle$.) Thus, the upper bound is slightly more tight for $\langle p_{12} \rangle$, whereas the lower bound is for $\langle P \rangle$.

In Fig. 2a, b, we find that the momenta $\langle p_{12} \rangle$ and $\langle P \rangle$ lie approximately at the center of the upper and lower bounds for all the atoms. We have therefore examined possible correlations of $\langle p_{12} \rangle$ and $\langle P \rangle$ with the mean values, $\langle p_> \rangle$ and $\langle p_> \rangle/2$, respectively, of the two bounds. Figure 3a, b shows that there are good linear correlations between $\langle p_{12} \rangle$ and $\langle p_> \rangle$ and between $\langle P \rangle$ and $\langle p_> \rangle/2$. A regression analysis gives

$$\langle p_{12} \rangle \cong 1.049859\langle p_> \rangle + 0.080069\,, \tag{11a}$$

$$\langle P \rangle \cong 1.047595\frac{\langle p_> \rangle}{2} - 0.009166\,, \tag{11b}$$

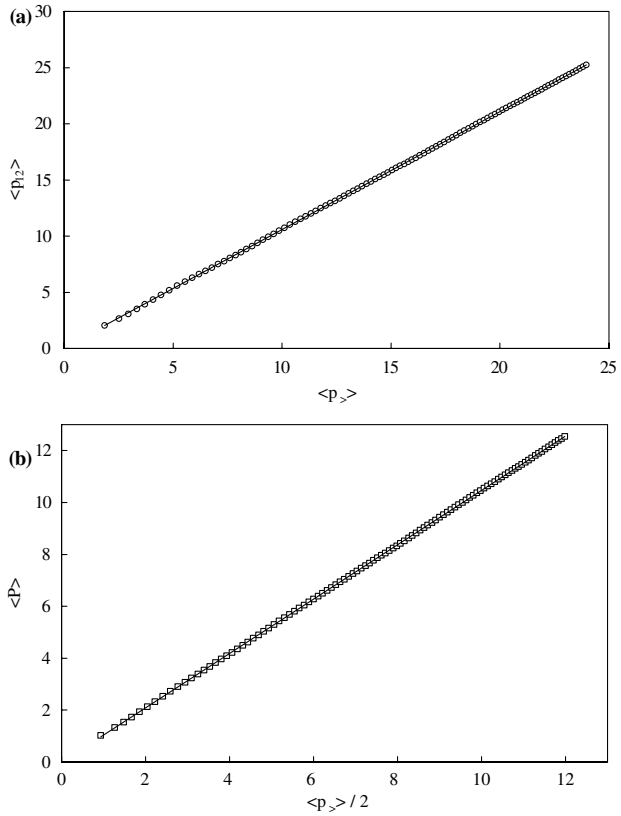

Fig. 3 Linear correlations between electron-pair momenta and the high momentum. **a** $\langle p_{12}\rangle$ and $\langle p_{>}\rangle$. **b** $\langle P\rangle$ and $\langle p_{>}\rangle/2$

with correlation coefficients 0.999990 and 0.999993. The correlation is slightly better for the latter. In Eqs. (11a) and (11b), the two linear coefficients are close to unity and the two constant terms are close to zero. Then, it is anticipated that the electron-pair momenta $\langle p_{12}\rangle$ and $\langle P\rangle$ are simply approximated by the high momentum $\langle p_{>}\rangle$ and its half, respectively. The anticipation is found to be true: The high momentum $\langle p_{>}\rangle$ is only 5.38% smaller than $\langle p_{12}\rangle$ and $\langle p_{>}\rangle/2$ is only 4.43% smaller than $\langle P\rangle$, when averaged over the 102 atoms.

5 Concluding remarks

Explicit consideration of any two electrons has shown that the average electron momentum $\langle p\rangle$ is the arithmetic mean of the low $\langle p_{<}\rangle$ and high $\langle p_{>}\rangle$ momenta. For the 102 atoms He through Lr in their ground states, the momenta $\langle p_{<}\rangle$ and $\langle p_{>}\rangle$ have been systematically examined at the Hartree–Fock limit level and the low momentum $\langle p_{<}\rangle$ has been found to be more sensitive to the electronic configuration than $\langle p\rangle$ and $\langle p_{>}\rangle$. The electron-pair relative $\langle p_{12}\rangle$ and center-of-mass $\langle P\rangle$ momenta are bounded from above by the sum $\langle p_{>}\rangle + \langle p_{<}\rangle$ and from below by the difference $\langle p_{>}\rangle - \langle p_{<}\rangle$ of the two momenta. The high momentum $\langle p_{>}\rangle$ has good linear correlations with the electron-pair momenta $\langle p_{12}\rangle$ and $\langle P\rangle$.

All the present theoretical results are valid both at the nonrelativistic and relativistic levels, though the numerical results are demonstrated within the nonrelativistic framework. When the relativistic effect is included, the three momenta $\langle p_{<}\rangle$, $\langle p\rangle$, and $\langle p_{>}\rangle$ are expected to increase in a parallel manner due to the so-called relativistic contraction of orbitals. For the relativistic change of the tightness of the inequalities, however, we have to await future examinations, as no relativistic electron-pair momenta are reported in the literature. When the electron correlation is included, it is expected that $\langle p_{<}\rangle$ decreases and $\langle p_{>}\rangle$ increases due to the radial correlation in momentum space. We wish to report such correlation effects in a quantitative manner, when appropriate wave functions are available for a group of atoms.

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